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RESEARCH PAPER

Phosphorus fractions of fertiliser-derived P in an allophanic soil under *Pinus radiata* seedlings grown with broom and ryegrass

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Abstract: Changes in phosphorus (P) fractions in a P deficient allophanic soil under *P. radiata* seedlings grown with broom (*Cytisus scoparius* L.) and ryegrass (*Lolium multiflorum)* in pots were studied 14 months after the application of triple superphosphate at the rates of 0, 50, and 100 $\mu g \cdot g^{-1}$, to determine the fate of fertiliser-derived P in the rhizosphere soils. Application of P fertiliser increased NaOH-P_i, NaOH-P_o, and H_2SO_4-P_i concentrations in the soil, but decreased the residual-P concentration. The resin-P_i concentration, which is extremely low in this soil (1 to 3 $\mu g \cdot g^{-1}$), remained the same. The majority of the added fertiliser P was however recovered in the NaOH-P_i fraction (40%–49%). This is due to the high P fixation in this soil (92%). The second highest P recovery was in NaOH-P_o fraction (7%–19%). Under P deficient condition or addition at the rate of 0 $\mu g \cdot g^{-1}$, the NaOH-P_i concentration in the radiata rhizosphere soil was lower than that in the bulk soil and broom and grass rhizosphere soils. This may be due to higher oxalate production by the roots and mycorrhiza under P deficient conditions which released some of the P fixed to the soils in the rhizosphere, which needs to be tested in future studies.

Keywords: *Cytisus scoparius*; *Lolium multiflorum*; phosphorus fertiliser; *Pinus radiate*; rhizosphere; soil phosphorus fractions

Introdction

In New Zealand forest plantations, phosphorus (P) is an important nutrient as most of the soils are P deficient or marginally deficient, and the element has been routinely applied appropriately since the 1960's (Hunter et al. 1991; Payn et al. 1998). The fate of applied fertiliser P at specified periods in forest soils can be examined by determining changes in the concentration of various soil P fractions based on their solubility in chemical reagents (Chang & Jackson 1957; Williams et al. 1967; Hedley et al. 1982a; Perrott et al. 1989; Tiessen & Moir 1993; Short et al. 2007). Many studies have reported the effect of P fertiliser application on P fractions in pasture soils (Rowarth & Tillman 1992; Rowarth et al. 1992; Perrott & Mansell 1989; Perrott et al. 1992). However, only few studies have been reported on determining the effect of P fertiliser application on P fractions in radiata pine forest soils (Chen et al. 2002; Chen et al. 2003; Condron et al. 1996). In addition, the studies in field conditions are focused mainly on determining the total organic and inorganic P pools without further separating the P fractions in each of these pools (Davis 1995; Parfitt et al. 1994).

Competition for nutrients (antagonism) is a mechanism by which the growth rate of forest trees is reduced by understorey vegetation (Nambiar et al. 1984; Smethurst & Nambiar 1989). Therefore, intensive vegetation management practices, with heavy emphasis on herbicide use, are typical in the establishment of *P. radiata* plantations. In contrast, Richardson et al. (1996) reported that some species of grass, herbaceous broadleaves and buddleia have significantly increased P concentrations in needles of 3-year-old radiata pine trees (synergism), but broom, gorse, lotus and pampas had no significant effect on needle P concentrations when they were grown in a moderately fertile soil in the field (Richardson et al. 1993). However, the effects of these plant species on soil P changes due to these understorey species were not reported.

An evidence of interaction between radiata pine seedlings and lucerne (*Medicago sativa* L.) in their effects on soil P dynamics, when they were grown together in a glasshouse trial, was reported by Scott (2002). He found that total P appeared to be depleted more under radiata pine seedlings grown with lucerne than under radiata, lucerne or ryegrass grown alone. He also found that when radiata seedlings were grown with lucerne, there was a significant redistribution of P from less labile to more labile fractions. Scott's study was conducted on a low P-fixing soil having a high concentration of plant-available P (Olsen P 17 $\mu g \cdot g^{-1}$) in

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the South Island of New Zealand. In the North Island, many of the radiata plantations are grown on P-deficient and high P-fixing soils developed on volcanic ash or pumice material (Hunter et al. 1991; Hewitt 1992). Under these conditions the interactions of radiata and understorey for P uptake may be different.

Recently, radiata pine silvicultural regimes in the country have become more intensive with a typical regime including understorey vegetation management, wider tree spacing with lower initial stocking of *P. radiata*, and application of P fertiliser (Gadgil et al. 1988; Payn et al. 2000). These changes in management regime have created a need for more information on soil P dynamics under radiata pine trees in association with other plants is required to create decision support systems to assist P fertiliser management. In the present study, we examined the changes in soil P fractions, following the application of three rates of Triple superphosphate (TSP) to an allophanic soil under *P. radiata* seedlings grown with broom (*Cytisus scoparius* L.) and ryegrass (*Lolium multiflorum)* under glasshouse condition.

Materials and methods

Experimental design and treatments

The experiment was arranged in a split-plot design inside a glasshouse. The main-plot treatments were three rates of P fertiliser: 0, 50, and 100 mg·kg^{-1} soil (equivalent to 0, 50 and 100 kg·ha^{-1}, bulk density = 1 g·cm^{-3}, depth = 10 cm) applied as TSP (granules ground to pass through 250 μm; total P = 20.7%) to the soil. Each main-plot was split into four split-plots consisting of four plant combinations (Fig. 1): (1) broom alone (compartment 1), and (2) radiata with ryegrass (compartment 2) (plants in both split-plot treatments grown within the same tray, but (1) and (2) separated by a nylon mesh (43 μm opening) to stop plant roots from one compartment getting into the other); (3) ryegrass alone (compartment 1), and (4) broom with radiata (compartment 2) (grown within the same tray, but (3) and (4) separated by a nylon mesh as carried out for plant combinations (1) and (2)). The treatments were replicated five times. This study employed the divided pots design using below-ground partitions to get the expected root interferences (Pannel 1993), meanwhile the above-ground environment for all pots was homogeneous as the order of the plants in every pot was similar. The experiment was designed in such a way to compare the effects of below-ground interaction of radiata + ryegrass and radiata + broom on phosphorus fractions in the bulk and rhizosphere soil.

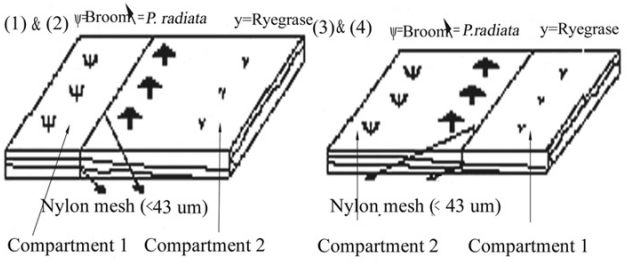

Fig. 1 Plant combinations in trays (pots)

A bulk sample of soil collected from Kaweka forest, New Zealand (from a 0–10 cm depth) was used in this trial. This forest area had not received fertiliser for at least 30 years. The soil is classified as Orthic Allophanic Soil (Cryands and Udands, Soil Taxonomy) (Hewitt 1998).

The soil was air-dried and passed through a 5-mm sieve to remove debris. A subsample of soil was ground to pass through a 2-mm sieve and analysed for chemical properties and soil plant-available P. The results are shown in Tables 1 and 2.

Table 1. Properties of the Allophanic Soil prior to planting in the glasshouse trial

Parameter	Value	Parameter	Value
pH (H_2O)	5.7	Na ($cmol_c·kg^{-1}$)	0.12
Bray-2 P ($μg·g^{-1}$)	3	CEC ($cmol_c·kg^{-1}$)	14
SO_4 ($μg·g^{-1}$)	29.3	N (%)	0.27
K ($cmol_c·kg^{-1}$)	0.29	C (%)	5.6
Ca ($cmol_c·kg^{-1}$)	2.9	P ret. (%)	92
Mg ($cmol_c·kg^{-1}$)	0.58		

Table 2. Phosphorus fractions in the soil. The soil is classified as Orthic Allophanic Soil and collected from Kaweka forest, New Zealand (from a 0–10 cm depth)

Parameter	Value	Parameter	Value
Resin-P_i ($μg·g^{-1}$)	1	H_2SO_4-P ($μg·g^{-1}$)	17
NaOH-P_i ($μg·g^{-1}$)	39	Residual-P ($μg·g^{-1}$)	61
NaOH-P_o ($μg·g^{-1}$)	130	Total P ($μg·g^{-1}$)	248

Planting and maintenance of the trial

Rectangular plastic trays having internal dimensions of 245 mm wide, 307 mm long, and 130 mm deep were used to grow the plants. Each tray (pot) was partitioned into two compartments having 1/3 and 2/3 of tray volumes separated by a nylon mesh with 43 μm openings, which was sealed with glue to the edges and bottom of the trays. The nylon mesh was expected to stop entry of roots and most of the mycorrhizal hyphae from one compartment to the other. After 4.5 kg of air-dried soil (Water content = 50%, equal to 3 kg oven-dried basis) was mixed homogeneously with the appropriate amounts of TSP, 1/3 and 2/3 of the soil weight was placed into compartments 1 and 2, respectively in the trays (pots).

Radiata seeds obtained from Forest Research Ltd., Rotorua were germinated according to the following procedure: seeds were soaked overnight on December 10, 2001 in running tap water, planted in moist perlite in a box with a lid (box of 10 cm depth), and kept in a dark place at 22–24°C. All the seeds germinated in seven days.

A week after germination of the seeds, three radiata seedlings were transplanted into compartment 2 in each tray on December 26, 2001. At the same time, 10 broom seeds (obtained from Forest Research Ltd.) were sown directly (after soaking five minutes in hot water at approximately 95°C) into compartment 1 or compartment 2 depending on the treatment and a week later the seedlings were thinned to four plants per tray. Four months later, ryegrass (variety Moata) seeds were sown and seven days after they germinated the seedlings were thinned to 10 plants per tray.

Five months after the planting of the radiata seedlings, a complete but –P (without P) nutrient solution (Middleton & Toxopeus 1973) was added to all trays. The nutrient solution was applied at a rate of 450 ml per tray four times during a two-week period, except for the nitrogen stock solution that was applied only two times. Applications of nutrient solutions were made at intervals of 3–4 days. In total, each tray received 54.2 mg N per kilogram soil (equivalent to 54 kg·ha^{-1}) and 35 mg K per kilogram soil (equivalent to 35 kg ·ha^{-1}).

The glasshouse was maintained at 28°C maximum and 13°C minimum temperatures. Soil water content was maintained at 80% field capacity by bringing the weight of tray and soil to the required weight by adding distilled water (field capacity of Kaweka forest soil was 87% gravimetric moisture content). The weight of soil in each tray at 80% field capacity was 5.1 kg. Broom, ryegrass, and radiata were harvested 56 weeks after planting.

Soil sampling

The root-soil mass was shaken gently and the fallen soil mass was collected. This represented the bulk (bk) soil. The soil adhering to the roots after the bulk soil had fallen away was collected by aggressively shaking the roots (Adamo et al. 1995; Wang & Zabowski 1998). This soil represented the rhizosphere (rh) soil. Each main-plot treatment (P fertiliser rates) had four bulk soils and six rhizosphere soils, which are referred to as:

- bulk soil from broom alone (compartment 1 (B_1-bk))
- rhizosphere soil from broom alone (compartment 1 (B_1-rh))
- bulk soil from radiata grown with grass (compartment 2 ($R_2 + G_2$-bk))
- rhizosphere soil from radiata grown with grass (compartment 2 (GR_2-rh))
- rhizosphere soil from grass grown with radiata (compartment 2 (RG_2-rh))
- bulk soil from broom grown with radiata (compartment 2 ($B_2 + R_2$-bk))
- rhizosphere soil from broom grown with radiata (compartment 2 (RB_2-rh))
- rhizosphere soil from radiata grown with broom (compartment 2 (BR_2-rh))
- bulk soil from grass alone (compartment 1 (G_1-bk))
- rhizosphere soil from grass alone (compartment 1 (G_1-rh)).

All soil samples were passed through a 2-mm sieve to remove debris and stored at 4°C for measuring P fractions.

Chemical analysis

Sample for the determination of soil pH was the suspension with a soil:water (w/w) ratio of 1:2.5. Soil suspensions were stirred and kept overnight at 20°C±2°C after which pH was determined using a pH meter equipped with a glass electrode (Blakemore et al. 1987). The organic matter content of the soils (expressed as percentage carbon) was determined by heating the samples in a stream of high purity oxygen in a Leco furnace to produce CO_2. The CO_2 concentration was measured with an infrared detector (Leco Co. 1996) and the quantity of the gas used to determine the total organic carbon. Cation exchange capacity (CEC) and exchangeable cations were determined by ammonium acetate leaching at pH 7 (Blakemore et al. 1987). The concentrations of K, Ca, Mg, and Na in the leachates were determined by atomic absorption spectrometry (AAS), and the ammonium concentration was determined using an Autoanalyser.

Phosphorus retention (an index of P fixation) was determined by measuring the P concentration in soil solution after 5-g soil was shaken with 25 ml solution containing P of 1000 μg·ml^{-1} for 16 h. Bray-2 P was determined by shaking 2.5 g of air dry soil for one minute in 25 ml of a solution containing 0.3 M NH4F and 0.1 M HCl and by measuring the P concentration in the solution by the colorimetric technique of Murphy & Riley (1962) (Blakemore et al. 1987). Soil P was fractionated using the method of Hedley et al. (1994) (Table 3) by first extracting 0.5 g air-dried soil with a cation (Na^+-form) and anion (HCO_3^- form) exchange resin membrane to determine resin-P, followed by 0.1 M NaOH extraction and determining inorganic P (NaOH-P_i) and labile organic P (NaOH-P_o) in the extract. The soil residue was further extracted with 0.5 M H_2SO_4 (H_2SO_4-P_i) followed by digestion of the residue with concentrated H_2SO_4 and H_2O_2 to determine the residual-P. The P concentrations in all the above extracts and digests were measured by the colorimetric technique of Murphy & Riley (1962). Plant uptake of P_i from the soil has been shown to be mainly from the resin-P_i fraction, but 0.1 M NaOH-P_i fraction can also supply P to plants in the long-term (Hedley et al. 1982a; Trolove et al. 2003). These two fractions can be grouped together and called labile-P_i.

Table 3. The P fractions measured in the sequential P-extraction procedure based on Hedley et al. (1994) and Short et al. (2007)

P fraction	Chemical nature of soil P
Resin-P_i	Inorganic P that is freely available to the plant
0.1 M NaOH-P_i	Inorganic P absorbed to Fe and Al hydrous oxides and allophane
0.1 M NaOH-P_o	Organic P absorbed to Fe and Al hydrous oxides and allophane
0.5 M H_2SO_4-P_i	Predominately calcium phosphates or apatite-type P minerals, some P occluded in Fe minerals
Residual-P	Recalcitrant inorganic P or structural and stable organic P in organo-mineral complexes

Statistical analysis

An analysis of variance (ANOVA) for a split-plot design was performed using SAS (SAS Institute 2001). The least significant difference (LSD) test at $p<0.05$, unless otherwise stated, was used to separate the means when the analysis of variance (ANOVA) results indicated that there were significant treatment effects (Steel et al. 1997). Resin P fraction data were square root transformed because the spread was proportional to the square root of the mean. H_2SO_4-P_i fraction data were $\log_e$ transformed because the spread was proportional to the treatment mean (Anon 2000; Steel et al. 1997).

Results

Resin-P_i

Neither the rates of P fertiliser addition nor the interaction of P rates and plant combination had any effect on resin-P concentration in the soil. Unlike P rates, plant combinations had a significant effect ($p<0.0001$) on the concentration of resin-P_i (Table 4).

The resin-P_i concentration in the rhizosphere soil of radiata in association with broom or grass (BR_2-rh, GR_2-rh) was significantly higher than that in the corresponding bulk soil (R_2+B_2-bk, R_2+G_2-bk), as well as in the rhizosphere soils of the associated plant (RG_2-rh and RB_2-rh). The resin-P_i concentration was also higher in broom and grass rhizosphere (RB_2-rh and RG_2-rh) than in the bulk soils (R_2+G_2-bk and R_2+B_2-bk) when they were grown in association with radiata (compartment 2).

Table 4. Effect of plant combinations on resin-P_i concentration in the soil

Sampling position	Resin-P_i ($\mu g \cdot g^{-1}$)*	Sampling position	Resin-P_i ($\mu g \cdot g^{-1}$)*
B_1-bk	1.67 b	R_2+B_2-bk	1.28 c
B_1-rh	1.76 b	RB_2-rh	1.84 b
R_2+G_2-bk	1.27 c	BR_2-rh	2.36 a
GR_2-rh	2.36 a	G_1-bk	1.77 b
RG_2-rh	1.86 b	G_1-rh	2.05 ab

Note: *Statistical analysis was carried out on $\sqrt{Y}$ transformed data.
Numbers followed by the same letters are not different at $p<0.05$.

NaOH-P_i

Unlike the resin-P_i concentration, the 0.1 M NaOH-P_i concentration in both the bulk and rhizosphere soils under all plant combinations significantly (p=0.0012) increased with increased rates of P fertiliser application (Table 5). There were significant differences ($p<0.0001$) in 0.1 M NaOH-P_i concentration between plant combinations as well. The interaction effect of fertiliser rates and plant combination on the 0.1 M NaOH-P_i concentration was also significant ($p<0.0001$) (Table 6).

Table 5. Main effect of P fertiliser on the NaOH-P_i concentration in the soil

P rate ($\mu g \cdot g^{-1}$)	NaOH-P_i ($\mu g \cdot g^{-1}$)
0	46.4 c*
50	69.1 b
100	91.1 a

*Numbers followed by the same letters are not different at $P<0.05$

Table 6. Effect of the P fertiliser rate and plant combinations on NaOH-P_i concentration in the soil

Sampling position	P fertiliser rate ($\mu g \cdot g^{-1}$)		
	0	50	100
B_1-bk	39.1 c*	68.6 ab	70.4 e
B_1-rh	50.0 a	63.8 b	74.8 e
R_2+G_2-bk	48.8 abc	64.9 b	96.6 bc
GR_2-rh	39.7 bc	74.0 ab	95.6 bcd
RG_2-rh	51.1 a	67.2 ab	99.0 b
R_2+B_2-bk	46.9 abc	64.4 b	88.7 cd
RB_2-rh	48.1 abc	70.5 ab	90.7 bcd
BR_2-rh	45.4 abc	73.8 ab	85.7 d
G_1-bk	49.6 ab	67.4 ab	99.2 b
G_1-rh	45.3 abc	76.6 a	110.7 a

*Numbers under each P rate followed by the same letters are not different at $P<0.05$

NaOH-P_o

The labile P_o (NaOH-P_o) was the largest P pool in the soil, containing 127 to 146 $\mu g \cdot g^{-1}$ soil (48% to 54% of the total soil P concentration). Increased rates of P fertiliser application significantly (p=0.012) increased the NaOH-P_o concentration in soils (Table 7). There were significant ($p<0.0001$) differences in the concentration of NaOH-P_o between plant combinations. The interaction between the P fertiliser rate and plant combination was also significant (p=0.011) (Table 8).

Table 7. Main effect of P fertiliser on NaOH-P_o concentration in soil

P rate ($\mu g \cdot g^{-1}$)	NaOH-P_o ($\mu g \cdot g^{-1}$)
0	123.1 b*
50	127.9 b
100	142.1 a

*Numbers followed by the same letters are not different at $P<0.05$

Table 8. Effect of the P fertiliser rate and plant combinations on NaOH-P_o concentration after 54 weeks growth in the soil in the glasshouse

Sampling position	P rate ($\mu g \cdot g^{-1}$)			Sampling position	P rate ($\mu g \cdot g^{-1}$)		
	0	50	100		0	50	100
B_1-bk	134 a*	121 c	165 a	R_2+B_2-bk	120 abc	128 bc	141 bc
B_1-rh	118 bc	123 c	147 b	RB_2-rh	115 c	123 c	141 bc
R_2+G_2-bk	123 abc	126 c	127 c	BR_2-rh	114 c	126 c	144 b
GR_2-rh	123 abc	116 c	138 bc	G_1-bk	131 ab	147 a	152 ab
RG_2-rh	120 abc	128 bc	128 c	G_1-rh	134 a	142 ab	139 bc

*Numbers within each P rate followed by the same letters are not different at $P<0.05$

H_2SO_4-P_i

Increased P rates significantly (p=0.0002) increased the concentration of H_2SO_4-P_i in the soil (Table 9), but the magnitude of the increase was lower than that of NaOH-P_i (Table 6) and NaOH-P_o (Table 8). The effects of plant combinations and the interaction of P fertiliser rates and plant combinations on H_2SO_4-P_i concentrations were also significant (p=0.0001 and p=0.0487, respectively) (Table 9).

Table 9. Effect of the P fertiliser rate and plant combinations on H_2SO_4-P_i concentration in the soil

Sampling position	P fertiliser rate ($\mu g \cdot g^{-1}$)*		
	0	50	100
B_1-bk	15.5 ab	18.9 ab	19.9 d
B_1-rh	14.0 b	18.9 ab	20.6 cd
R_2+G_2-bk	15.3 ab	20.3 ab	25.3 ab
GR_2-rh	16.4 a	20.6 ab	25.7 ab
RG_2-rh	15.0 ab	18.8 b	24.8 ab
R_2+B_2-bk	15.1 ab	19.6 ab	22.9 bc
RB_2-rh	15.6 ab	19.6 ab	23.7 b
BR_2-rh	16.3 a	21.1 a	23.9 b
G_1-bk	15.0 ab	20.2 ab	27.2 a
G_1-rh	15.8 a	20.0 ab	28.0 a

*Statistical analysis was carried out on $\log_e$ (Y) transformed data.
Numbers within each P rate followed by the same letters are not different at $P<0.05$.

Residual-P

P fertiliser addition at the rates of 50 and 100 $\mu g \cdot g^{-1}$ soil significantly (p=0.0150) decreased the concentration of residual-P from 45 to 41 $\mu g \cdot g^{-1}$ soil (Table 10). The actual magnitude of this de-

pletion is, however, small. The effect of plant combinations on the concentration of residual-P in the soil was also significant (p=0.0248), but the magnitude of the effect was very small (Table 11). There was no significant interaction between the P fertiliser and plant combinations on the residual-P concentration.

Table 10. Effect of P fertiliser on residual-P concentration in the soil

P rate (μg·g^{-1})	Residual-P (μg·g^{-1})
0	45.0 a*
50	41.0 b
100	40.9 b

*Numbers followed by the same letters are not different at P<0.05

Table 11. Effect of plant combinations on residual-P concentration in soil

Sampling position	Residual-P (μg·g^{-1})	Sampling position	Residual-P (μg·g^{-1})
B_1-bk	41.3 cd*	R_2+B_2-bk	42.1 abcd
B_1-rh	40.3 d	RB_2-rh	39.2 d
R_2+G_2-bk	41.7 bcd	BR_2-rh	41.4 bcd
GR_2-rh	45.8 a	G_1-bk	44.4 abc
RG_2-rh	42.1 abcd	G_1-rh	45.1 ab\

*Numbers followed by the same letters are not different at P<0.05

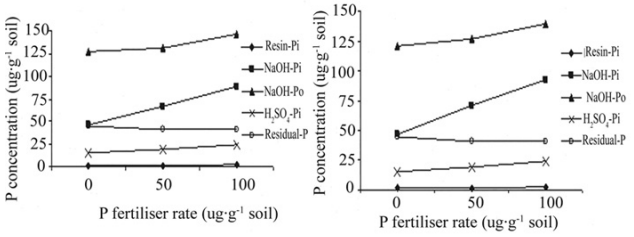

Fig. 2 Comparison of the change in P concentration in the different soil P fractions with an increase in the P fertiliser rate in (a) the bulk soil, and (b) the rhizosphere soil, averaged over all treatments

Table 12. The % recovery of added P in each of the P fractions in the bulk and the rhizosphere soils averaged over all plants*

P fraction	Bulk soil P fertiliser rate (μg·g^{-1})		Rhizosphere soil P fertiliser rate (μg·g^{-1})	
	50	100	50	100
Resin-P_i	0.3	0.8	0.3	1.0
NaOH-P_i	40.4	42.6	48.8	46.1
NaOH-P_o	7.0	19.2	11.4	18.9
H_2SO_4-P_i	9.1	8.6	8.6	8.9
Residual-P	-7.4	-4.5	-8.2	-3.7
Total	49.4	66.7	60.9	71.2

* (P concentration(μg·g^{-1} soil) in fertilized soil − P concentration in control soil)/fertiliser P (μg·g^{-1} soil) ×100

Proportion of fertiliser P in the different soil P fractions

The soil P fractionation at plant harvest showed that the P concentration in the different P fractions decreased in the order of NaOH-P_o > NaOH-P_i > residual-P > H_2SO_4-P_i > resin-P_i in both the bulk and the rhizosphere soils averaged over all treatments (Fig. 2). The pattern of change in P concentration in the different P fractions, as the P fertiliser rate was increased, was the same for the bulk and the rhizosphere soils. Increased P fertiliser rates increased the concentration of NaOH-P_i, NaOH-P_o, and H_2SO_4-P_i fractions in the soil, decreased the concentration of residual-P and had no effect on the concentration of resin-P_i. The recovery of P added in fertiliser in the different soil P fractions, in both the bulk and the rhizosphere soils averaged over all plant combinations, ranged from 49% to 71% (Table 12).

Discussion and conclusion

Resin-P_i

The resin-P_i concentration in the soils ranged from 0.9 to 2.6. μg P·g^{-1} soil. This range is approximately close to the resin-P_i concentration values of 1.9 to 4.6 μg·g^{-1} soil reported for Waikare clay loam soil from the north of Auckland, New Zealand (Comerford et al. 2002). However, this range is much lower than the resin-P_i concentration values of 30 to 45 μg·g^{-1} soil reported for many other forest soils in USA (Spears et al. 2001). It was expected that resin-P_i concentration would increase with P rates because the soil had low plant-available P. The reason for the resin-Pi concentration not increasing with increased rates of P addition is the high fixation of the added P by this Allophanic Soil (Clark & McBride 1984; Parfitt 1989). The higher resin-P_i concentration in the rhizosphere soil of radiata in association with broom or grass (BR_2-rh, GR_2-rh) compared with that in the corresponding bulk soil (R_2+B_2-bk, R_2+G_2-bk), as well as that in the rhizosphere soils of the associated plant (RG_2-rh and RB_2-rh) is probably related to organic anions (especially oxalate) released by radiata roots, which would have mobilized P in the rhizosphere (Malajczuk & Cromack 1982; Fox & Comerford 1992; DeLucia et al. 1997). Increase of P availability following a decrease in soil pH has been reported by Hedley et al. (1982a) in a study with rape (*Brassica napus* Var. Emerald) fertilised with KH_2PO_4 (Hedley et al. 1982b). They explained that the increased P availability with a decrease in rhizosphere pH was due to an enhancement of P dissolution from acid-soluble forms of soil P_i.

Some studies have shown that the resin-P_i concentration is lower in the rhizosphere than in the bulk soils because of the depletion of P in the rhizosphere by plant uptake (Trolove et al. 1996; Zoysa et al. 1998). The fact that resin-P_i is higher in the radiata rhizosphere in the current study indicates that the rate of P mobilisation in the rhizosphere was higher than the rate of P depletion by radiata. The reason for the higher resin-P_i concentration in broom and grass rhizosphere (RB_2-rh and RG_2-rh) compared with that in the bulk soils (R_2+G_2-bk and R_2+B_2-bk) when they were grown in association with radiata (compartment 2) is probably due to the influence of the root processes of radiata and not that of grass or broom because there was no difference in resin-P_i between rhizosphere and bulk soils of broom (B_1-rh vs B_2-bk) or grass (G_1-rh vs G_2-bk) when they were grown alone (compartment 1). These results are consistent with the findings of Fisher & Stones (1969) which showed that conifers increased available P in soils beneath or near the conifers, and this resulted in a significant increase in P concentration in

herbaceous plants beneath the conifers.

NaOH-P_i

As Kaweka soil contains allophane and hence has a high P fixing capacity (Table 1), most of the fertiliser-P added would have been fixed to the soil (Clark & McBride 1984; Parfitt 1989) and this is reflected in the increase in NaOH-P_i concentration with an increase in rate of P application. The NaOH-P_i concentration increased at a faster rate with P rates under grass, rather than under broom, when these plants were grown alone (compartment 1). The rate of increase of NaOH-P_i with an increased P rate in soils under radiata in association with grass (compartment 2) is also higher than that under radiata in association with broom (compartment 2) (Table 6). These differences in the rate of increase of NaOH-P_i are related to the difference in the growth rates of grass and broom. Broom grew at a faster rate with increased rates of P application than grass. This plant per pot utilized a higher amount of applied P than grass (10.7 $\mu g \cdot g^{-1}$ vs 2.9 $\mu g \cdot g^{-1}$) (Rivaie 2005) leaving lower quantities of the added P in the soil.

The interaction of plant combinations and P rate was significant for NaOH-P_i in the rhizosphere of grass and radiata when zero P treatment was compared with other P rates. The concentrations of 0.1 M NaOH-P_i in rhizosphere soils of radiata (GR_2-rh and BR_2-rh) were approximately the same as in the rhizosphere soils of the two associated plants (RG_2-rh and RB_2-rh) for the P application rates of 50 and 100 $\mu g \cdot g^{-1}$. But when no P fertiliser was applied (P deficient conditions), the NaOH-P_i concentration was significantly lower in the radiata rhizosphere soil (GR_2-rh) than in the rhizosphere soil of grass (RG_2-rh) in compartment 2. This is probably because under P deficient condition, the radiata root mycorrhizae is most active in producing oxalates (Malajczuk & Cromack 1982; DeLucia et al. 1997) which may have released Pi fixed to allophane and Fe and Al oxides resulting in a decrease in NaOH-P_i concentration in rhizosphere soils. This suggestion needs to be tested in future radiata rhizosphere studies. The NaOH-P_i concentration in the rhizosphere of broom was, however, not higher when compared to that in radiata when no P was applied. This is perhaps due to the higher uptake of P by broom compared to that by grass (Rivaie 2005).

NaOH-P_o

The results of the present study show that the soil used in the trial had NaOH-P_o (127 $\mu g \cdot g^{-1}$ and 50.2% of total P) as the largest P fraction. However, the extent of increase in NaOH-P_o concentration with increased P fertiliser rates is lower than that of the NaOH-P_i concentration. This shows that the proportion of P applied to the soil that was converted to the labile organic P pool was less than what was absorbed to allophone and Fe + Al oxides.

The increase in NaOH-P_o concentration with an increase in P rates could be due to increased root growth (Rivaie 2005) which might have increased soil organic matter content from the decay of dead roots and hyphal materials. Condron & Goh (1989) reported that a significant proportion of P in superphosphate, applied annually for 20 years to a Lismore silt loam (Udic Ustochrept) soil under intensively grazed irrigated pasture, was converted to organic P. They suggested that this was probably related to the biological immobilization of soil inorganic P via plant, animal and microbial residues.

The interaction between the P fertiliser rate and plant combinations was demonstrated below. When no P was applied (0 TSP), the concentration of NaOH-P_o in the rhizosphere soil of broom grown alone (B_1-rh) was significantly lower than that in the bulk soil (B_1-bk) (Table 8), while, the NaOH-P_i concentration was higher in broom rhizosphere soil than in the broom bulk soil (Table 6). This suggests that under P deficient conditions the phosphatase enzyme in the rhizosphere was very active and it converted labile organic P to inorganic P (Tarafdar & Junk 1987), which was mostly fixed to allophone in this soil. This trend was, however, not observed at high rates of P (Table 8) although, at a 100 TSP treatment, the NaOH-P_o concentration was again lower in the broom rhizosphere than in the broom bulk soil. There was no significant difference in the NaOH-P_o concentration between the bulk and rhizosphere soils of radiata and grass. However, Liu et al. (2004) reported that under field conditions the NaOH-P_o concentration was higher in the rhizosphere of radiata than in the bulk soil. He explained this difference as due to a higher concentration of organic carbon as a result of long-term root and hyphae decomposition in the rhizosphere.

The NaOH-P_o concentrations in the radiata rhizosphere soils were not different from those in the rhizosphere soils of the associated plants and the corresponding bulk soils. This is consistent with the phosphatase activity results in Rivaie (2005) study where no difference was observed between radiata rhizosphere soils and the associated plant rhizosphere soils. There was also no difference in the effect of plant species on NaOH-P_o concentrations in radiata rhizosphere (GR_2-rh vs BR_2-rh). However, Scott (2002) reported that total organic P extracted in lucerne-tree rhizosphere soil under field conditions was significantly less than ryegrass-tree soil and this lower P concentration was associated with a higher level of phosphatase enzyme activity (acid and alkaline) and phosphodiesterase activity.

H_2SO_4-P_i

When TSP is applied to soil, part of the monocalcium phosphate in TSP is converted to dicalcium phosphate at the soil/fertiliser interface. In the long term these phosphates get converted into mostly amorphous Fe, Al-phosphates and trace amounts of Ca-phosphates (Lehr et al. 1959). The H_2SO_4 extraction gives a measure of this calcium-bound P. The interaction between the P fertiliser rates and plant combinations on H_2SO_4-P_i concentrations is explained below. At 0 and 100 $\mu g \cdot g^{-1}$ rates of application, the concentration of H_2SO_4-P_i was significantly lower in the rhizosphere soil of broom alone, than in the rhizosphere soils of radiata and grass alone (B_1-rh vs GR_2-rh, BR_2-rh and G_1-rh). This is probably because of the higher growth rate of broom compared to that of radiata and grass (Rivaie 2005) resulting in higher amounts of plant uptake of Ca from the broom

rhizosphere thus decreasing the Ca-bound P extracted by H_2SO_4. Such difference in H_2SO_4-P_i concentration was not observed for the 50 $\mu g \cdot g^{-1}$ rate. The values were generally lower in the rhizosphere of broom, but were not statistically significant.

Residual-P

The increased residual-P depletion at increased rates of P fertiliser application suggests that the added P in fertiliser had not entered the residual-P pool, but, to the contrary, plants have mobilized some of the residual-P by the increased growth of roots and mycorrhizae resulting from higher plant growth at higher P rates. Plants are reported to improve their accessibility to total soil P resources through the increased absorption area of the root system (Barber 1995) or increased association with mycorrhizae (Marschner & Dell 1994; Brandes et al. 1998). Plant uptake of P from the residual-P fraction has been reported in literature. For example, Gahoonia & Nielsen (1992) reported that 15−18% of total P depletion by rape grown on sandy silt loam soil, fertilised with a complete nutrient solution, was from the residual-P fraction in the soil.

The residual-P concentration in the rhizosphere soil of radiata grown with broom (BR_2-rh) was lower than that in the rhizosphere soil of radiata grown with grass (GR_2-rh). Also, broom alone (B_1-bk, B_1-rh) had a lower residual-P concentration than grass alone (G_1-bk, G_1-rh). These differences are consistent with the differences in the growth rate between grass and broom (Rivaie 2005). Broom had a higher growth rate than grass, and, therefore, extracted more residual-P. Scott (2002) also reported that radiata grown with lucerne in an Immature Pallic Soil produced a greater decline in the recalcitrant P pool (the difference between total P concentration and total inorganic P concentration) than when radiata was grown alone, lucerne grown alone, ryegrass grown alone and radiata grown with ryegrass. He explained that this was due to a higher P uptake by radiata and lucerne as a result of the greater total biomass production when they were grown together.

Proportion of fertiliser P in the different soil P fractions

Application of P fertiliser increased NaOH-P_i, NaOH-P_o, and H_2SO_4-P_i concentrations in the soil, but decreased the residual-P concentration. The resin-P_i concentration remained the same. The NaOH-P_i fraction constituted the highest percentage of P (40−49%) derived from the added P fertiliser. This is due to the very high P retention capacity (92%) of the Allophanic Soil used in this study (Clark & McBride 1984; Parfitt 1989). Even though P fixation in the soil is high, some of this fixed P can be available to plants. The next highest P recovery was in the NaOH-P_o fraction (7%−19%) (Table 12). This fraction, though not immediately available to plants, may become available in the long-term.

Unlike the findings of Trolove et al. (1996) and Zoysa et al. (1997) on soils with low P fixing capacities, in this study the P recovery of fertiliser P in the resin-P_i pool is extremely low (≤ 1%) due to the high P fixing capacity of this soil (Table 12). The above workers reported P recoveries in the resin-P_i pool of 13% to 30%.

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